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REPORT ON METHODS FOR MAPLE PRODUCTS

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In the 1953 report of the Associate Referee, it was pointed out that there is no satisfactory analytical method by which maple products can be analyzed to establish their purity. Since that report a paper by Albert Cholette and Marcel Jean (presented at the Second Maple Products Conference, Philadelphia, November 1953) was published in the Journal of this Association.[1] This paper reported a study of the effectiveness of methods ordinarily used to detect adulterations of maple sirup. The study showed that while conductivity and malic acid values were the best criteria, they were still unsatisfactory. Conductivity will not detect the presence of less than 1.1 parts of white sugar or 4 parts of brown sugar to 1 part of maple sugar. Malic acid values will not detect less than 4.6 parts of white sugar or 7.2 parts of brown sugar to 1 part of maple. Cholette and Jean pointed out that as little as 0.62 parts of white sugar or 0.94 parts of brown sugar to 1 part of maple could be detected by K_2O values, and as little as 0.25 parts of brown sugar to 1 part of maple by P_2O_5 values. On the basis of their report it was decided to test these methods as criteria for the purity of maple sugar in the 1954 collaborative studies. Since collaborative studies on methods for the determination of K_2O and P_2O_5 in maple sirup had never been made it was hoped that the current study would (*a*) indicate the effectiveness of K_2O and P_2O_5 values as criteria of purity, and (*b*) show the reliability of the different methods used in the analysis of maple sirups for these constituents.

Samples.—Both brown and white cane sugars were used as maple sirup adulterants. To minimize the number of samples used in this study a 50–50 mixture of brown and white sugar was used as the adulterant. Three sirup samples, designated A, B, and C, were prepared and sent to the collaborators for analysis.

Sample B, a pure maple sirup, was a mixture of equal parts of U. S. AA and U. S. B grades. Sample A consisted of 90 parts of B and 10 parts of the 50–50 cane-brown sugar sirup of the same density as the maple sirup.

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1 *This Journal*, 37, 939 (1954).

Sample C consisted of 75 parts of B and 25 parts of the 50–50 cane-brown sugar sirup.

Analysis of Samples.—The collaborators were requested to analyze the three sirups for K_2O and P_2O_5 by any method they wished. In addition they were asked to determine the specific conductance of the sirups, since this is the analytical constant most commonly used, and the degrees Brix of the sirups by refractometry.

RESULTS

Eleven collaborators participated in these studies and the results are tabulated in Tables 1, 2, 3, and 4; n is the number of values reported by a collaborator; $\bar{x}$, the mean of his values; $\bar{\bar{x}}$, the mean of the $\bar{x}$'s; $s_{\bar{x}}$, the standard deviation of the means; M, the median value of the $\bar{x}$'s; and t, calculated Student's t value and $t_{0.05}$ (t values at the 95 per cent level for a given number of degrees of freedom).

P_2O_5 Analysis.—The eleven collaborators reported 29 values for

TABLE 1.—*P_2O_5 analysis*

COLLABORATOR	METHOD[a]	SAMPLE A		SAMPLE B		SAMPLE C	
		n	$\bar{x}$	n	$\bar{x}$	n	$\bar{x}$
			per cent		per cent		per cent
0	II	1	0.0016	2	0.00059	2	0.0028
1	I	1	0.0014	1	0.00060	1	0.0028
3	II	2	0.0021	2	0.00098	2	0.0030
4	II	4	0.0016	4	0.00083	4	0.0034
5	II	2	0.0041	2	0.00210	2	0.0070
6	I	4	0.0016	4	0.00070	4	0.0038
7	II	3	0.0017	3	0.00077	3	0.0030
12	II	2	0.0050	2	0.00300	2	0.0090
13	II	2	0.0016	3	0.00073	2	0.0030
14	III	4	0.0015	4	0.00073	4	0.0027
15	II	2	0.0016	2	0.00080	2	0.0030
M			0.0016		0.00073		0.0030
$\bar{\bar{x}}$			0.00216		0.00107		0.0040
$s_{\bar{x}}$			0.0012		0.00076		0.0021
Omitting Nos. 5 and 12:							
$\bar{\bar{x}}$			0.00163		0.00074		0.00306
$s_{\bar{x}}$			0.0002		0.00012		0.0003
B *vs* C: $t = 21.39$							
A *vs* B: $t = 11.48$							
$t_{.05} = 2.12$							

[a] I = Colorimetric, modification of method of DICKMAN and BRAY (*Anal. Chem.*, 12, 665 (1940).
II = Colorimetric (*Official Methods of Analysis*, 7th Ed., 6.38, 6.39, and 6.40).
III = Colorimetric, modification of method of KING (*Biochem. J.*, 26, 292 (1932).

TABLE 2.—*K_2O analysis*

COLLABORATOR	METHOD[a]	SAMPLE A		SAMPLE B		SAMPLE C	
		n	$\bar{x}$	n	$\bar{x}$	n	$\bar{x}$
			per cent		*per cent*		*per cent*
0	I	1	0.16	2	0.15	2	0.17
1	II	3	0.16	3	0.15	2	0.17
3	III	2	0.19	2	0.18	2	0.21
4	III	4	0.18	4	0.17	3	0.19
5	III	2	0.15	2	0.15	2	0.17
6	I	4	0.18	4	0.16	4	0.35
7	III	3	0.13	3	0.12	3	0.14
12	III	2	0.17	2	0.18	2	0.18
13	III	3	0.18	3	0.16	3	0.18
14	IV	3	0.14	4	0.14	4	0.16
15	III	2	0.18	2	0.17	2	0.19
M			0.17		0.16		0.18
$\bar{\bar{x}}$			0.17		0.16		0.192
$s_{\bar{x}}$			0.021		0.018		0.056
A *vs* B: $t=1.20$							
B *vs* C: $t=1.24$							
$t_{.05}=2.09$							

[a] I = Flame analysis of the ash.
II = Lithium dipicrylaminate (*Anal. Chem.*, 26, 727 (1954).
III = Chloroplatinate (*Official Methods of Analysis*, 7th Ed., 6.16, 6.17, and 6.19).
IV = Sodium cobaltinitrite (*Med. Res. Council Special Report*, Series No. 213 (1936) London).

TABLE 3.—*Degrees Brix*

COLLABORATOR	SAMPLE		
	A	B	C
0	67.1	65.7	67.1
1	66.9	65.8	67.2
3	67.6	65.9	67.6
4	66.7	66.1	66.7
5	67.4	65.7	67.5
6	67.6	65.8	67.5
8	67.4	65.8	67.1
12	67.2	65.3	66.7
13	67.9	65.8	67.4
14	68.4	66.9	68.4
15	67.7	66.2	67.5
M	67.4	65.8	67.5
$\bar{\bar{x}}$	67.4	65.9	67.3
$s_{\bar{x}}$	0.47	0.40	0.47

TABLE 4.—*Conductivity values*

COLLABORATOR	SAMPLES		
	A	B	C
0	114	109	118
1	107	103	114
5	105	100	112
6	105	102	113
8	123	118	131
14	125	121	134
M	109.6	106	116
$\bar{\bar{x}}$	113	109	120
$s_{\bar{x}}$	9.1	8.9	9.7

A *vs* B: $t = 0.74$
B *vs* C: $t = 1.98$
$t_{.05} = 2.23$

sample A, 31 for B, and 29 for C. The values were obtained by three different methods. All values are reported on the sirup basis, since apparently the error in weighing the sample for the analysis is less than in the Brix determination (Table 4). By inspection it appears that the values for samples A, B, and C reported by collaborators 5 and 12 are high by some constant factor. Since it was not possible to check the cause of this discrepancy with the collaborators at the time of writing this report, two analyses of the data are presented: one in which all of the data are included and the other from which the values of collaborators 5 and 12 are omitted. Considering only the second case, the M values for all of the data for each of the samples is in close agreement with the $\bar{\bar{x}}$ values. The three methods of analyses are apparently equally reliable since they yielded combined values with low standard deviations.

A comparison of the $\bar{\bar{x}}$'s obtained for the three samples shows by visual inspection that there is a marked difference between the $\bar{x}$'s and the $\bar{\bar{x}}$ values for sample B (the pure sirup) and those for A (the 10 per cent adulterated) and C (the 25 per cent adulterated). This observation is confirmed by Student's t test which shows these differences to be significant.

These data indicate that it would be a relatively simple matter to demonstrate small percentages of adulterants, provided the adulterants were the same as those used in this year's study and the value for P_2O_5 in pure sirup was similar to that obtained for sample B and of a fixed value. Unfortunately, this is not the case; the values for P_2O_5 in pure maple sirup cover a fairly wide range. Dr. Marcel Jean of Laval University has reported a range of 0.00013 to 0.00183 per cent (sirup basis). This range was established from the analysis of 35 pure maple sirups. By

plotting the P_2O_5 $\bar{x}$ values for samples A, B, and C (Fig. 1) it is seen that while the values for A, B, and C are well separated, those for A and B fall within the area bounded by lines o and o', Jean's limits for P_2O_5 values for pure maple sirups. Sample C is the only one which would seem to be adulterated.

This observation indicates that the full range of P_2O_5 values, like other analytical constants used to establish the purity of maple sirup, are too wide and that two ranges for each constant should be used: one to cover the full range of values (when the analytical value of the test sirup falls outside of this range, it provides positive presumptive evidence of adul-

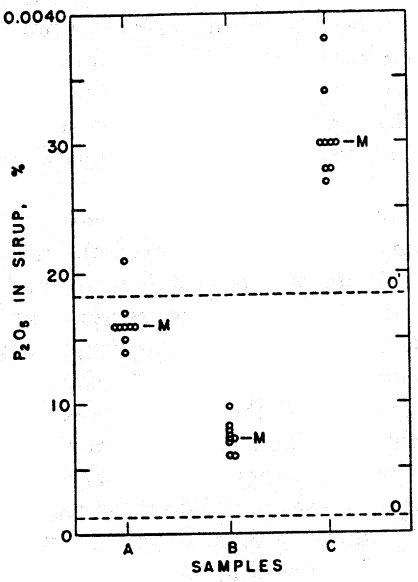

FIG. 1.—$\bar{x}$ values for P_2O_5 of pure (B) and adulterated (A, C) maple sirup.

teration) and the other to be a much narrower range and include only those values representing the confidence limits ($\bar{s} \pm t_{0.05}S/\sqrt{n}$). Any value falling outside of this narrower or confidence limit range, but within the boundaries of the full range of value for pure sirup, would be interpreted as presumptive evidence.

K_2O Analysis.—As in the case of the P_2O_5 analyses, 11 collaborators reported 89 K_2O values for the three maple sirup samples, A, B, and C. These values are shown in Table 2. Unlike the P_2O_5 values, inspection shows no pronounced difference between the collaborators' means ($\bar{x}$'s) or their grand averages ($\bar{\bar{x}}$'s) for B, the pure sirup, 0.16 per cent, and for A and C, the two adulterated samples which are 0.17 and 0.19 per cent, respectively. This observation is confirmed by the Student's t test which shows that there is no significant difference between the means for A and B or B and C.

The analyses were made by four different methods, and the precision as determined by the standard deviation of the means of each collaborator's results indicates that all of the methods have merit. As a means for establishing the purity of adulterated samples, such as the ones reported here, they have no merit. As pointed out by Cholette and Jean, they should prove to be of value for the evaluation of samples containing large proportions of sucrose as the adulterant.

Degrees Brix.—The degrees Brix for each of the three sirup samples was determined by refractometry. Table 3 shows the average, $\bar{x}$, of each of the eleven collaborators' results. This analysis was requested to provide information as to the precision with which the degrees Brix could be measured. These results indicate (standard deviation, $s_{\bar{x}}$)that a precision of little better than $\pm 0.5°$ can be expected. It is therefore questionable whether analytical values, derived from weighed sirup samples, should be converted to a dry weight basis by using refractometric readings as conversion factors. For this reason all results given in this report are on a sirup basis.

Conductivity Values.—The collaborators were asked to measure the conductance of the three sirup samples so that a comparison with the P_2O_5 and K_2O values could be made. While only six collaborators had the equipment to make conductivity measurements, their results show the non-validity of this method as a criterion of purity of maple sirup. Regardless of whether the comparison is made between individual collaborator's means, $\bar{x}$'s, or between the grand averages of the collaborators' means, $\bar{\bar{x}}$'s, the differences between the values for the two adulterated samples (A and C) and those for the pure sirup are not significant. Even more important, the mean conductivity values of the two adulterated samples A and C fall safely within these limits, indicating them to be pure; whereas the grand average $\bar{\bar{x}}$ of the values for the pure sirup is one unit low.

Here, as with the P_2O_5 values, the situation might be greatly improved if (*a*) the conductivity values of pure maple sirup were re-established, and (*b*) the range of these values was narrowed by setting confidence limits.

Unlike the values for P_2O_5 and K_2O, the conductance values are influenced by the *p*H of the sirup. Perhaps the relationship of *p*H to conductivity values of pure maple sirups should be studied and correlated.

CONCLUSIONS AND RECOMMENDATIONS

1. Conductivity and K_2O values are unreliable as criteria of purity of maple sirup.

2. For certain types of adulterations, P_2O_5 values tend to give reliable measurements that would serve as criteria of purity of maple sirup.

3. The range of analytical values of maple sirup should be narrowed by expressing the range in terms of confidence limits. Analytical values

falling outside of the confidence limits but within the maximum range would give good presumptive evidence of adulteration.

It is recommended*—

(1) That further studies be made of the P_2O_5 and the K_2O methods as criteria of purity of maple products.

(2) That the limits of K_2O and P_2O_5 analytical values be established by the analysis of a large number of *pure* maple sirup samples taken from various regions.

(3) That the limits of conductance values be re-established, giving attention to *p*H effects.

(4) That confidence limits be established for analytical values used as criteria of purity of maple sirup.

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* For report of Subcommittee D and action of the Association, see *This Journal*, 38, 88, 89 (1955).